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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: POROUS CATALYTIC SYSTEM FOR OLIGOMERISING LIGHT OLEFINS

(57) Abstract: The present invention relates to the use of a silicon-based porous catalytic system for oligomerising light olefins said porous silicon-based catalytic system having an average pore diameter of between about 1 nm and about 5 nm and an acidity level of between about 150 µmol/g and about 650 µmol/g, and prepared from at least one hydrolysable silicon-based compound, or other source of silicon, and at least one non-ionic surface active agent. The invention also relates to a process for oligomerising light olefins using said silicon-based porous catalytic system, and to certain silicon-based porous catalytic systems.







tional Application No PCT/EP 03/14857

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 B01J21/12 B01J23/46 B01J29/02

B01J23/42

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According to International Patent Classification (IPC) or to both national classification and IPC

#### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  $IPC \ 7 \ B01J$ 

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/131930 A1 (LIU YU ET AL) 19 September 2002 (2002-09-19) the whole document	1-11, 19-35, 43-47
Υ	US 5 270 273 A (PELRINE BRUCE P ET AL) 14 December 1993 (1993-12-14) column 3, line 37 - column 17, line 10; claims; examples; tables	1-48
Α	EP 0 272 496 A (ENIRICERCHE S.P.A.) 29 June 1988 (1988-06-29) the whole document	
Υ	US 6 204 424 B1 (PUJARI AJIT ATMARAM ET AL) 20 March 2001 (2001-03-20) column 2, line 36 - column 5, line 20; claims; examples; tables	1–48

Further documents are listed in the continuation of box C.	Patent family members are listed in annex.
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the International filling date  "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" tater document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  "&" document member of the same patent family
Date of the actual completion of the international search  9 July 2004	Date of mailing of the international search report
Name and mailing address of the ISA  European Patent Office, P.B. 5818 Patentlaan 2  NL – 2280 HV Rijswijk  Tel. (+31-70) 340-2040, Tx. 31 651 epo ni,  Fax: (+31-70) 340-3016	Authorized officer  de Cauwer, R



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	Citation of designant with indication where an analysis of the relevant	Indoor do do do
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 299 855 B1 (CARRAZZA JOSE ET AL) 9 October 2001 (2001-10-09) column 2, line 53 - column 9, line 35; claims; examples; tables	20-24
		,

Form PCT/ISA/210 (continuation of second sheet) (January 2004)



rnational application No. PCT/EP 03/14857

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)
This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:
Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
2. Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).
Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)
This International Searching Authority found multiple inventions in this international application, as follows:
see additional sheet  As a result of the prior review under R. 40.2(e) PCT, part additional fees are to be refunded.
As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. X As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:  1–48
4. No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
Remark on Protest  The additional search fees were accompanied by the applicant's protest.  No protest accompanied the payment of additional search fees.

### FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: Claims 1-11, 19-35 and 43-47 (in as far as they relate to a substantial catalytic metal-free porous system)

A porous silicon-based catalytic system substantially free from catalytic metal; The use of said catalytic system for converting a light olefin feedstock into oligomer paraffins, and a process for converting a light olefin feedstock into oligomer paraffins using said catalytic system

2. claims: Claims 1-10, 12, 18, 19, 25-34, 36, 39 and 43-47 (in as far as they relate to a porous system containing catalytic metals chosen from groups 8,9 and 10)

The use of a porous silicon-based catalytic system containing one or more catalytic metals chosen from groups 8,9 and 10 for converting a light olefin feedstock into oligomer paraffins, and a process for converting a light olefin feedstock into oligomer paraffins using said catalytic system

3. claims: Claims 1-10, 12-15, 17-19, 25-34, 36-39, 41 and 43-47 (in as far as they relate to a porous system containing only platinum as catalytic metal)

The use of a porous silicon-based catalytic system containing platinum for converting a light olefin feedstock into oligomer paraffins, and a process for converting a light olefin feedstock into oligomer paraffins using said catalytic system

4. claims: Claims 1-10, 12-16, 18-19, 25-34, 36-40 and 43-47 (in as far as they relate to a porous system containing only rhodium as catalytic metal)

The use of a porous silicon-based catalytic system containing rhodium for converting a light olefin feedstock into oligomer paraffins, and a process for converting a light olefin feedstock into oligomer paraffins using said catalytic system

5. claims: Claims 1-10, 12-15, 18-19, 25-34, 36-39 and 42-47 (in as

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### FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

far as they relate to a porous system containing platinum and rhodium as catalytic metal)

The use of a porous silicon-based catalytic system containing platinum AND rhodium for converting a light olefin feedstock into oligomer paraffins, and a process for converting a light olefin feedstock into oligomer paraffins using said catalytic system

6. claim: Claim 48

Diesel fractions



## INTERNATIONAL SEARCH REPORT

Information on patent family members

Intertional Application No PCT/EP 03/14857

	atent document d in search report		Publication date		Patent family member(s)	Publication date
US	2002131930	A1	19-09-2002	US	6585952 B1	01-07-2003
00			10 03 2002	ÜS	2002018747 A1	14-02-2002
				MO	03053849 A1	03-07-2003
				AU	5297601 A	11-12-2001
				EP	1296894 A1	02-04-2003
				ĴΡ	2003535009 T	25-11-2003
				WO	0192154 A1	06-12-2001
				ÜS	2002182143 A1	05-12-2001
				US	2002187098 A1	12-12-2002
				US	2002187098 A1 2002182144 A1	
				US	2002162144 A1 2004067842 A1	05-12-2002
						08-04-2004
US 	5270273 	A	14-12-1993 	US 	5105051 A	14-04-1992
EP	0272496	Α	29-06-1988	IT	1213433 B	20-12-1989
				CA	1290495 C	08-10-1991
				DE	3765527 D1	15-11-1990
				DK	669387 A	24-06-1988
				EP	0272496 A1	29-06-1988
				JP	63168406 A	12-07-1988
				NO	875290 A ,1	
				US	5003125 A	26-03-1991
US	6204424	B1	20-03-2001	DE	19857314 A1	03-02-2000
				GB	2332155 A ,I	3 16-06-1999
				JР	3486566 B2	13-01-2004
				JP	2000042416 A	15-02-2000
US	6299855	В1	09-10-2001	US	6106802 A	22-08-2000
				US	5840271 A	24-11-1998
				BR	9900580 A	04-01-2000
				DE	29924407 U1	27-02-2003
				DE	69907530 D1	12-06-2003
				DE	69907530 T2	18-03-2004
				EP	0935996 A2	18-08-1999
				JP	3306387 B2	24-07-2002
				JP	11278827 A	12-10-1999
				US	6485702 B1	26-11-2002
				ZA	9901258 A	18-08-1999
				DE	19704875 A1	14-08-1997
				FR	2744933 A1	22-08-1997
				GB	2309967 A ,E	
				GB	2341853 A ,E	3 29-03-2000
					0100740 00	
				JP	3139740 B2	05-03-2001
				JP JP		05-03-2001 13-01-1998
					10007474 A 1005203 C2	13-01-1998 10-08-2000